Gated resistors with copper phthalocyanine films

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The material science offers more and more candidate materials to be applied in the industry of the electronic compounds. Unfortunately, many of them possess high toxicity for humans. Other are expensive or do not meet the technical expectations. This paper is focused on the copper phthalocyanine (CuPc) as a potential compound of low toxicity, electronic components. The synthesis of the CuPc dispersion is presented. By dip-coating this organic compound is deposited onto a ITO covered glass with a compatible insulator. The technology tries to find a transistor behaviour. The electrical tests show an intermediate component behaviour – a gated resistor. The average Source-Drain resistance is 22 GΩ, the positive gate voltage reduces the drain current. The gated resistor function is fulfilled.

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1. Introduction

Metal-phthalocyanines exhibit tetrapyrolic macrocycles of great importance in analytical and photochemical applications [1]. Peripheral and non-peripheral positions in the benzenoid ring of phthalocyanines can be substituted by many other molecules to award new features [2]. Therefore, a similar structure is encountered to chlorophyll and hemoglobin molecules. On the other hand, phthalocyanines and their derivatives have been identified with organic semiconductor [3], due to their conjugated heterocyclic aromatic molecules and the π-electrons delocalized system. Among these compounds, the copper phthalocyanine is one of the widely applied material for photodetectors, solar cells, optoelectronic devices [4]. Their good thermal and chemical stability, beside to the combined properties such as light resistance, resistance at temperature, coating strength and resistance to bases and acids recommend them to be applied in temperature or humidity sensors [5].

A prominent representative is the copper phthalocyanine (CuPc) having several crystalline structures, of which the most commonly observed are phase α and phase β. Rather the α-CuPc phase was applied in organic electronics, due to its physical properties such as carriers mobility and anisotropy [6, 7]. The β-CuPc phase has a spike-like aligned structure, having an angle of nearly 45° with the vertical axis. Changing the angle in the α-CuPc phase, a better overlap occurs of π-electrons in α-CuPc versus β-CuPc results, with a maximum conductivity of the crystalline phase α [8]. From the toxicity point of view, CuPc also called phthalocyanine blue or B15: 3 pigment is a blue organic pigment used in the ecologic textile industry or as the current organic pigment used in tattoo inks on the European market [9].

Modern procedures of the CuPc synthesis led to minimal wastes of PCBs (biphenyls, polychlorinated), usually sub - 25 ppm, as required by the Environmental Protection Agency [10]. These organic compounds in combination with nanoparticles were investigated for sensors and electronic structures [11-13]. For instance, Fasihbeiki and collaborators proposes in 2019 a solar cell composed by PET / Indium Tin Oxide (ITO) / active layer / Al [14]. The active layer consists in usual organic compounds PEDOT: PSS on enhanced MEH: PPV insulator [15], but with fullerene-C_{60} nanoparticles linked to benzothiadiazole [14]. The produced solar cells with nanoparticles increased its short circuit current up to 0.036 mA/cm^2 [14]. A low toxicity of the CuPc layers is a promising advantage to develop green electronic technologies in a next future.

Consequently, CuPc searches for some applications among the electronic components, in this paper. Simply deposited CuPc layers on a glass substrate offer an alternative to resistors. If a compatible insulator is deposited beneath the CuPc film, a component with insulated gate control can be performed. In the next sections, the material synthesis, beside to a simple device technology is depicted. Finally, the current-voltage experimental curves are extracted and interpreted.

2. The CuPc synthesis

The main substance, copper phthalocyanine is purchased from Sigma-Aldrich as insoluble blue powder. The synthesis protocol to obtain copper phthalocyanine dispersion involves the following stages of work:

• preparation of raw materials, quantitative washing and preparation of laboratory instruments;

• copper phthalocyanine blue powder is dispersed ultrasonically in DMSO (US - 40 min) to obtain a blue dispersion;

• the obtained solution is centrifuged at 4000 rpm for 3 min collecting the supernatant;

• the precipitate is again subjected to the dispersion in DMSO;

• the supernatant is centrifuged at 8000 rpm for 30 min, the operation is repeated if the supernatant is still blue;

• the blue precipitate re-disperses ultrasonically in the working solvent after three consecutive washings.

Ultrapure water 18.2 MΩ·cm was used in all washing or preparation stages. Finally, stable blue copper phthalocyanine dispersion is obtained.

3. CuPc deposition to achieve a sample of an electronic component

Indium-Tin-Oxide (ITO) coated glasses were purchased from Bruker Daltonics. They are used to be covered by the next organic layers. The previous CuPc dispersion is placed in a recipient able to allow a dip coating (DC) deposition method [16]. A multi-layered CuPc structure was accomplished on the ITO coated glass, in different areas, with different thicknesses. Onto the ITO layer, polystyrene was deposited as insulator, also by DC method. Then the CuPc film was deposited above using an extraction rate from recipient around of 50 ... 100 mm/min. Details of the applied DC method are explained elsewhere [17-19].

The electronic samples from this article were achieved by multilayer structures with different CuPc thicknesses. These thicknesses were obtained by successive DC extractions, with various depths of the sample sinking into recipient. The thicknesses of the CuPc layers from Fig. 1 are approximated by optical inspection to be: 150 nm, 300 nm, 450 nm.

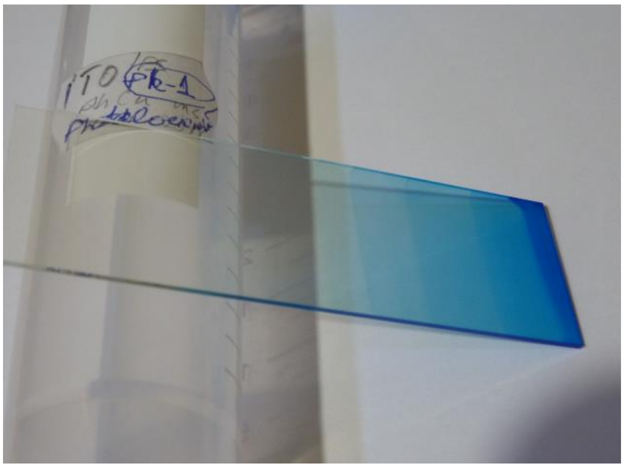


Fig. 1. The sample with copper phthalocyanine made in multilayered version with various thicknesses of organic films (color online)

In order to investigate a basic electronic component – the gated resistor, two thin probes are positioned by a mechanically controlled Signatone S-725 kit, onto the top of the CuPc film as Source and Drain contacts, while the ITO electrode acts as a back-gate contact [22]. A similar in situ characterization component is the pseudo-MOS transistor [20, 21] or the organic thin film transistors [23]. The challenge that we have to face is to establish if the main function of this CuPc component is a resistor, a gated resistor or a transistor.

We measure the current between two probes in direct contact with the CuPc film - Source and Drain and we investigate if the Gate voltage has any influence on the Drain current. The Source, Drain and Gate probes are selected to be long and flexible, to avoid the CuPc film penetration. We used gold wires from RioGrande-US with the code 14/20 yellow Gold-Filled round wires 21 Gauge 1-Hard. Additionally, the gold is selected as electrode, due to its low contact resistances on organic semiconductors, as other authors experimented [13, 23]. The fabricated CuPc sample is caught in the testbench of an optical microscope, Fig. 2. Connecting independently the drain and gate terminals from a double stabilized power supply HM8012, keeping the source grounded, the electronic component set-up is ready for measurements.

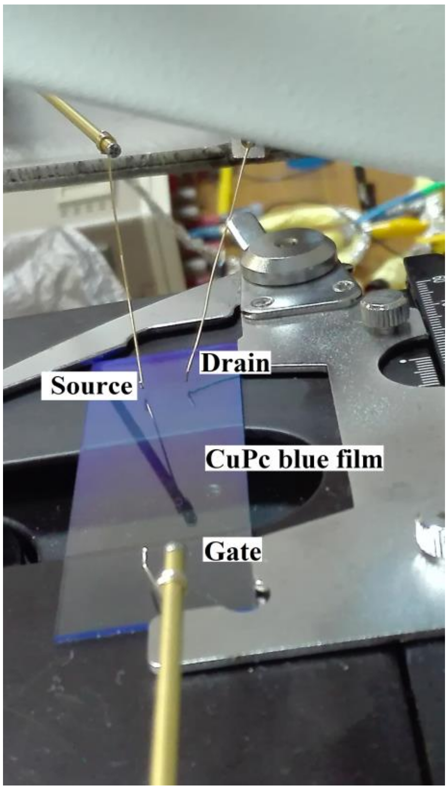
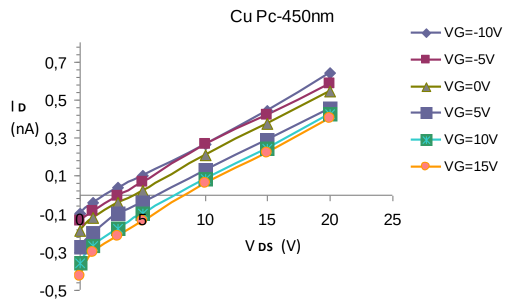


Fig. 2. The CuPc sample on the microscope testbench (color online)

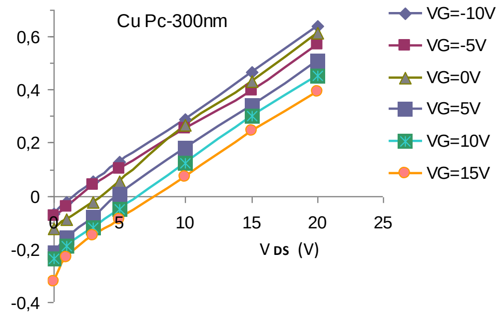
4. Electrical characterization of the CuPc samples

Each connected sample fulfils the function of an independent electronic component. When the Source and

Drain probes are placed onto the CuPc film with thinnest film of 150 nm, the tested component is noted by CuPc-150 nm. When the Source and Drain probes are placed onto the CuPc film with film of 300 nm or 450 nm, the tested component is noted by CuPc – 300 nm and respectively CuPc – 450 nm. The electrodes can be biased from 0 V to 20 V.

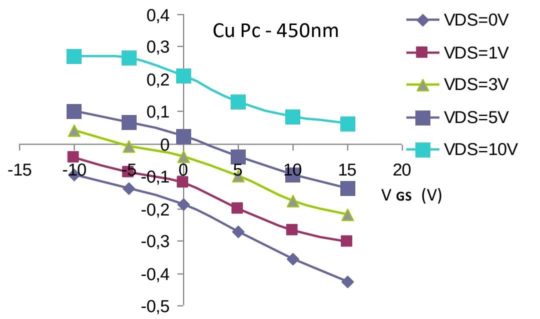


(a)

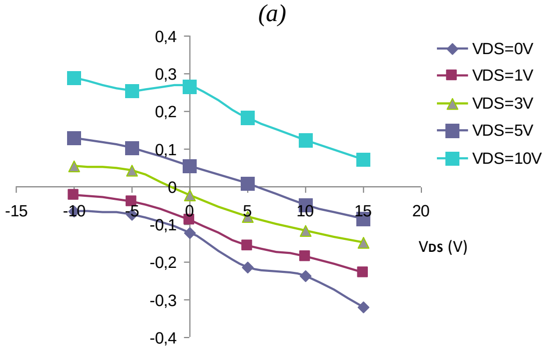


(b)

Fig. 3. (a) I_D-V_{DS} for the sample with PhCu 450 nm; (b) I_D-V_{DS} for the sample with PhCu 300 nm (color online)



(a)



(b)

Fig. 4. (a) I_D-V_{GS} for the sample with PhCu 450 nm; (b) I_D-V_{GS} for the sample with PhCu 300 nm (color online)

The drain current is measured by a Keithley6487 pico-ammeter. The gate current is monitored to be under the detection limit of the pico-ammeter. In this way, the polystyrene breakdown or CuPc film penetration by probes is surely avoided. The output characteristics measure the drain current versus the drain-source voltage at a given gate voltage, I_D-V_{DS}, for the thickest CuPc film (450 nm), Fig. 3a and for the median CuPc film (300 nm), Fig. 3b. The transfer characteristics measure the drain current versus the gate-source voltage at a given drain voltage, I_D-V_{GS}, for CuPc – 450 nm structure in Fig. 4a, or for CuPc - 300 nm structure in Fig. 4b.

The output characteristics show a quasi-linear behavior of the CuPc samples, indicating its application as a resistor than a transistor. An average value of the extracted resistance is 20 GΩ for the CuPc – 450 nm structure and increases up to 22 GΩ for the CuPc – 300 nm structure, till 24 GΩ for the CuPc – 150 nm structure. However, the I_D-V_{DS} curves indicate a non-null, but weak dependence with V_{GS}. For instance, at V_{DS} = 10 V, the current is I_D = 0.05 nA for V_{GS} = +15 V, while the current is I_D = 0.3 nA for V_{GS} = -10 V. So, the negative gate voltage produces higher currents. Hence, we expect to capture an p-type behavior of the CuPc film. Going further with measurements toward the transfer characteristics, for a given drain voltage (V_{DS} = 1 V), the drain current suffers variations at V_{GS} = -10 V from -0.03 nA (CuPc – 300 nm) or -0.045 nA (CuPc – 450 nm) up to -0.24 nA (CuPc - 300 nm) or -0.31 nA (CuPc – 450 nm) at V_{GS} = +10 V. The drain current variation with the gate voltage is not high, but always occurs (Fig. 4). Due to this reson and due to the linear current – voltage dependency, the electronic components that are tested on these samples fulfills a rolle of a resistor with a gate control. By a similitude with the devices know as gate diodes that is a pn junction separated by an insulator layer from a gate terminal [24], this CuPc test componnt is associated with a gated resistor. They are not simply resistors because the gate biasing modulates the drain current – a superior behavior to a resistor, as other authors claimed, too [25].

5. Discussions and comparisons

In order to compare our results with the other researchers, some experimental current – voltage curves are extracted from literature [26]. Studying novel materials for the electronic applications, Deb and collaborators have recently investigated the current – voltage measurements through thin films of silver nanostructured nanocomposite films. They change the silver ion concentration in the nanocompound from 1 mM to 5 mM to enlarge the maximum current from 2 nA respectively to 350 nA. In their case, the electrical resistance ranges from 15 GΩ to 60 MΩ that is close to our measurements. Fig. 5 comparatively presents our I_D-V_{DS} curves recorded from CuPc – 150 nm variant, for positive drain voltages, besides to picked curves from [26] at 1 mM and 5 mM.

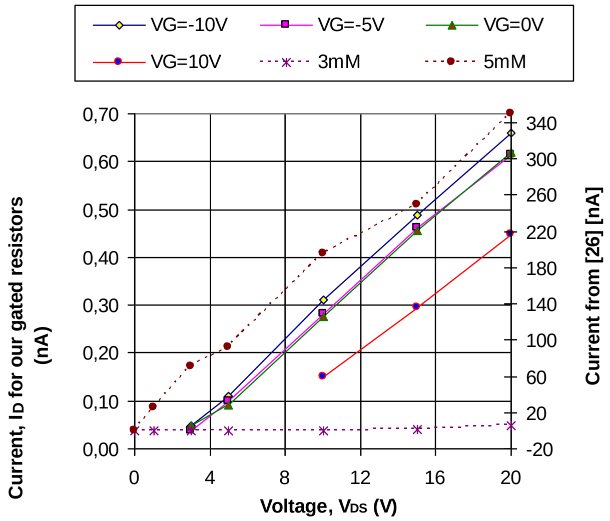
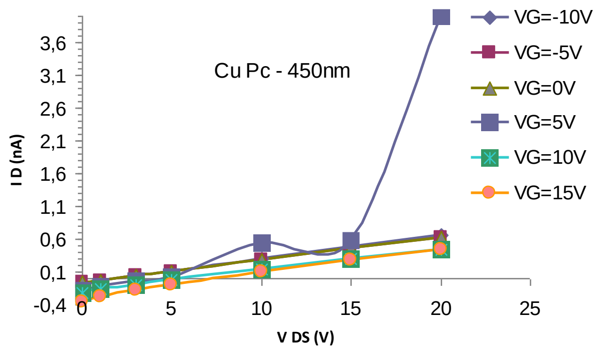
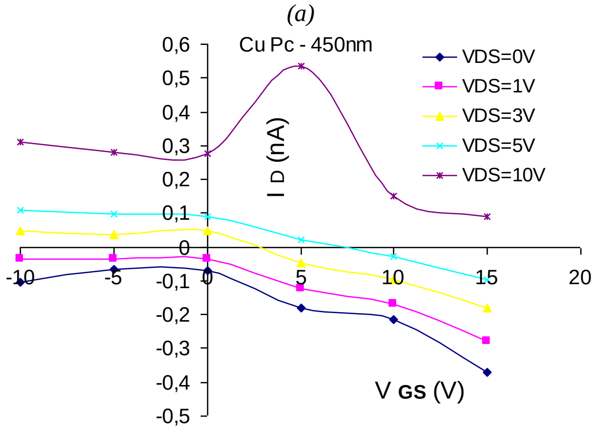


Fig. 5. Comparisons between I-V measured curves for CuPc - 150 nm gated resistor at different gate voltages and I-V curves from literature [26] at 3 mM and 5 mM silver ions concentration (color online)

From the extracted electrical resistance, taking into account that the aspect ratio of the probes has an area A = 0,15 nm^2 and a distance d = 3 mm between the upper probes, a conductivity of the CuPc film around 8 x 10^{-4} S/m can be estimated that is equivalent to a resistivity of 1,1 x 10^3 Ωm.



(a)



(b)

Fig. 6. (a) The output characteristics; (b) the transfer characteristics – of a second sample (color online)

Another index of the technology success is the repeatability and stability. Therefore, the same technological steps are repeated on another glass substrate. The main features of the static characteristics are preserved, especially on the structures CuPc – 150 nm and CuPc – 300 nm. For the structure CuPc – 450 nm some non-linear curves arise, but only at a given VDS or VGS, Fig. 6. a-b.

These deviations can be explained by obvious differences among structures, in terms of non-uniform surfaces, thicknesses variations, interface states and Source-Drain positioning.

If the curve at V_G = 5 V is removed from the output characteristics, the last curves are very similar to those from Fig. 3a. If the curve at V_D = 10 V is removed from the transfer characteristics, the last curve family are very similar to those from Fig. 4a. So the curves are stable and repeatable.

The CuPc applications in the actual electronic components consist in extremely high resistances, consuming low area, which are sometimes necessary in integrated circuits [27-31]. If, additionally, these resistances are controlled by the gate voltage, they can be used as sense detectors: for a fix V_{DS} = 3 V, if V_G < 0 V then I_D > 0, elsewhere I_D < 0 that it means it changes the sense. These sense detections are used in sensors and accelerometers [32]. These applications circumvent the general trends in flexible electronics [33], organic components [34] and interference among electronics, nanotechnologies and green organic compounds [35].

7. Conclusions

This paper reported an experimental set-up to test the copper phthalocyanine (CuPc) as a potential non-toxic compound for the industry of the electronic component. The synthesis of the CuPc dispersion was revealed. Then, a brief technology was depicted to achieve a minimal electronic device. In this scope, an ITO covered glass was coated by polystyrene, followed by CuPc layers with three thicknesses: 150 nm, 300 nm and 450 nm. Using two mobile probes onto the top of the structure as Source and Drain and ITO as the Back-Gate electrode, the I_D - V_{DS} and I_D - V_{GS} curves were extracted. All the curves possessed a good linearity, plus a drain current modulation by the gate biasing. So, the gated resistor function is fulfilled. Some comparisons with other similar situations from literature were presented, which sustain our gated resistors able to offer high values and to consume low area.

Acknowledgements

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